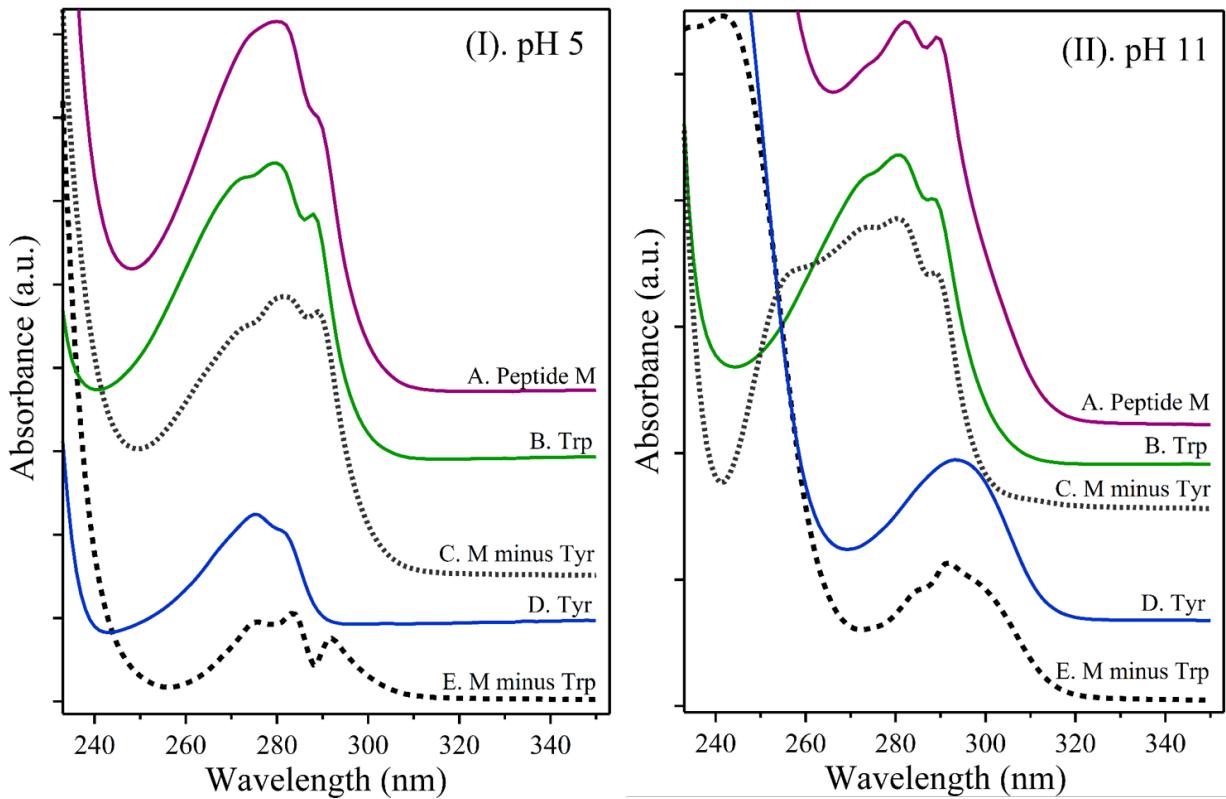
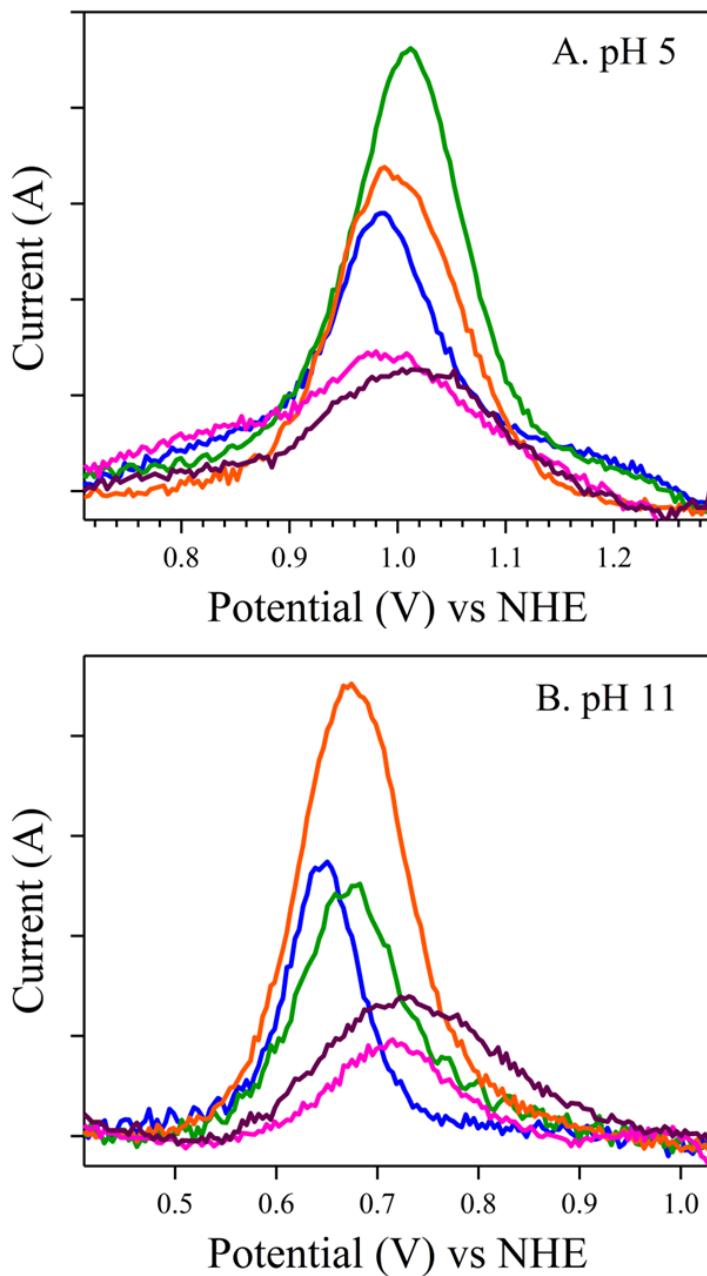


Supplementary Figure 1. NMR data. Selected region of $[^1\text{H}, ^1\text{H}]$ ROESY (A) and ^1H -NMR (B) spectra showing several long-range dipolar contacts between residues.

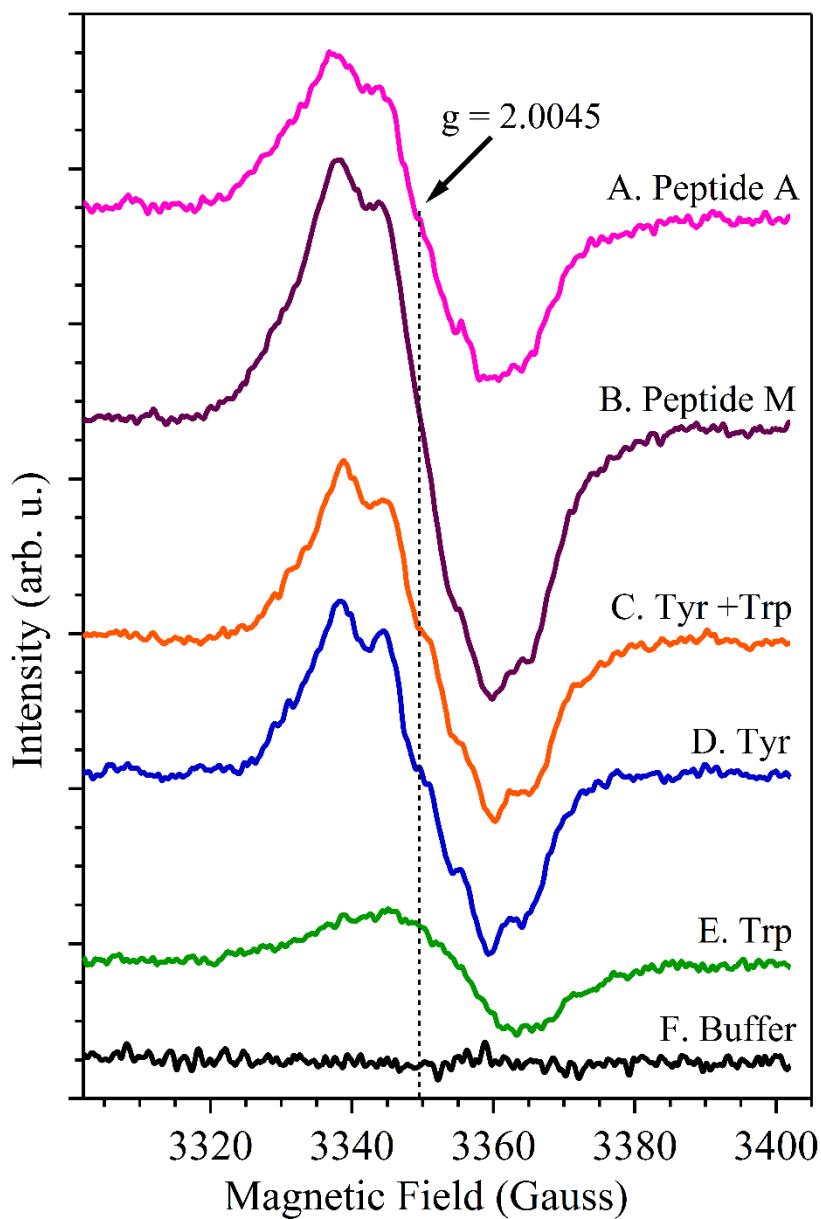


Supplementary Figure 2. UV absorption spectra. Data were derived from Peptide M (purple), tyrosine (blue) and tryptophan (green) at pH 5 (I) and at pH 11 (II). The gray dotted trace (C) was obtained by subtracting the tyrosine spectrum from that of Peptide M. The black dashed trace (E) was obtained by subtracting the tryptophan spectrum from that of Peptide M. The analyte concentration was 100 μ M, and the buffer contained 5 mM acetate, pH 5 (I) or 5 mM borate, pH (11). The spectra were averaged from two independent measurements. The tick marks denote 0.1 absorbance unit.

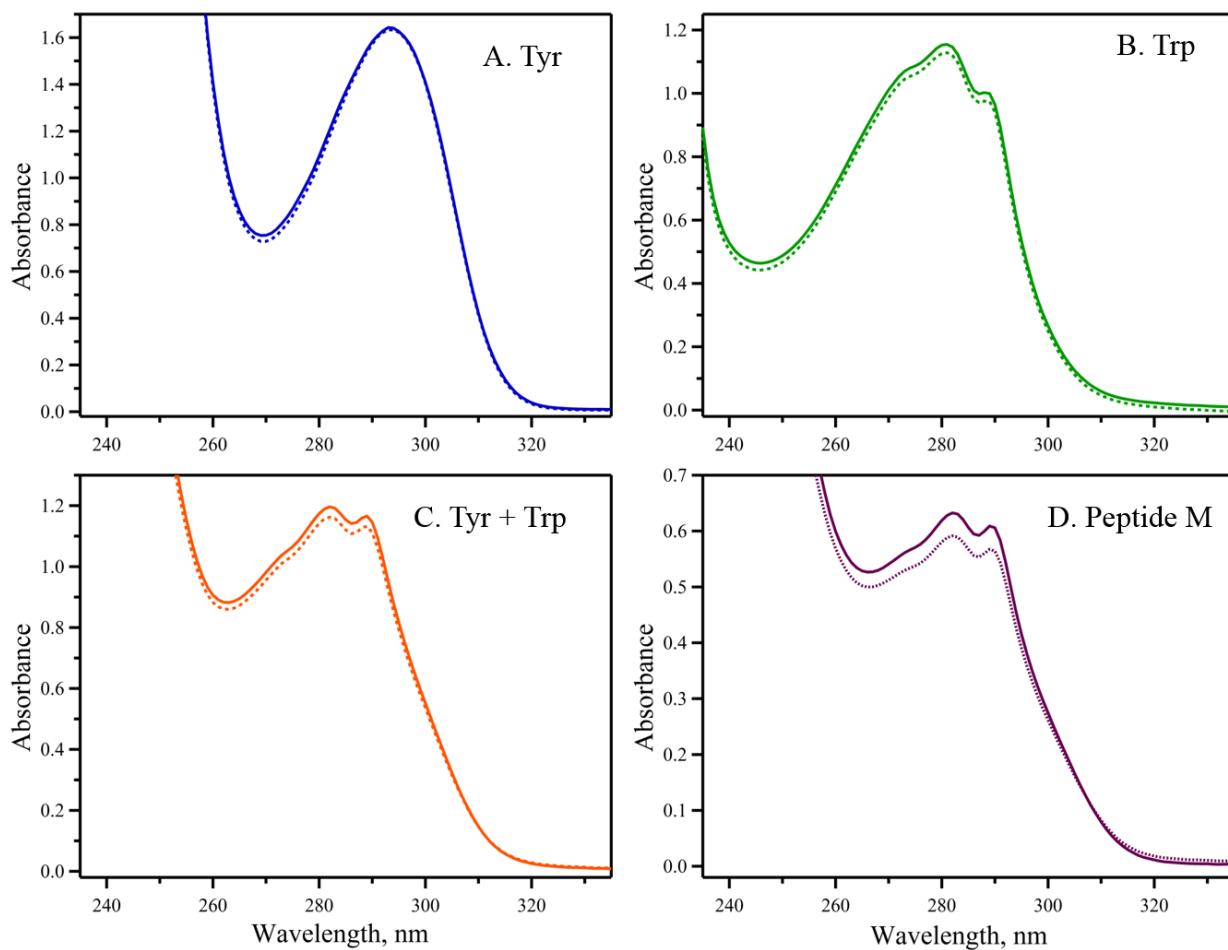


Supplementary Figure 3. DPV. Data were derived from Peptide A (pink), Peptide M (purple), a tyrosine-tryptophan solution (orange), a tyrosine solution (blue) and a tryptophan solution (green) at pH 5 (A) or at pH 11 (B). The data were baseline corrected for presentation purposes. The analyte concentration was 100 μ M. At pH 5, the buffer was 5 mM acetate, 200 mM KCl (A). At pH 11, the buffer was 5 mM borate, 200 mM KCl (B). The data were averaged from three independent measurements for peptides and from nine independent measurements for amino acid analytes. Potentials are given versus the normal hydrogen electrode (NHE) by adding 0.22 V to the values measured using a 1 M KCl-filled Ag/AgCl reference electrode. The tick marks denote 1×10^{-7} units. Peptide A (pink) and Peptide M (purple) voltammograms are multiplied by 2 for

clarity. DPV measurements were performed on a computer-controlled Princeton Applied Research 273A potentiostat. Experiments were conducted in an argon-sparged, three-electrode cell (CH Instruments, Austin, TX) equipped with a 3 mm glassy carbon working electrode, platinum wire counter electrode, and a Ag/AgCl reference electrode in 1 M KCl ($E = 0.22$ V (NHE)). Data were collected in increments of $\Delta E = 4$ mV at a scan rate of 32 mV/s. The differential pulse amplitude was 25 mV. Data were fit to a polynomial baseline using PeakFit 4 (Systat Software Inc, San Jose, CA) and smoothed using CorrView3 (Scribner, Southern Pines, NC). Data on the amino acids were averaged in triplicate and data on the peptides were averages of nine trials. The peak potentials reported in the text were determined from the centroid of the data before baseline correction. Hexamine ruthenium (III) chloride (200 μ M, 1 M KCl)¹ was used as standard in each trial and gave a peak potential of -0.200 ± 0.003 V versus Ag/AgCl (average of 20), as expected. In control experiments at pH 11, CAPS was used as a buffering agent. The substitution of the borate buffer by CAPS had no effect on the DPV measurement at pH 11.



Supplementary Figure 4. X-band EPR spectra. Data were acquired from Peptide A (A), Peptide M (B), tyrosine + tryptophan solution (C), tyrosine solution (D) and tryptophan solution (E). The buffer blank is shown in (F). EPR spectra^{2,3} were collected on a Bruker EMX spectrometer (Billerica, MA) at 160 K using the following conditions: microwave frequency, 9.2 GHz; microwave power, 200 μ W; modulation amplitude, 1 G; modulation frequency, 100 kHz; scan time, 168 s; number of scans, 4; time constant, 655 ms. Radicals were generated using 50 flashes at 266 nm (50-60 mJ) generated by a Nd-YAG laser (Continuum Surelite III, Santa Clara, CA). The analyte concentration was 1 mM, and the buffer contained 10 mM borate, pH 11. The data were averaged from three independent measurements. The tick marks denote 500 units.



Supplementary Figure 5. UV-Vis spectra. Data acquired from tyrosine (A), tryptophan (B), tyrosine-trypophan solution (C) and Peptide M (D) before (solid line) and after (dashed-line) EPR measurements. The solutions of tryptophan (B), tyrosine-trypophan mixture (C) and Peptide M (D) were diluted four fold before measurements due to the high absorbance of the original 1 M solution.

Supplementary Table 1. Resonance assignments of 1H chemical shifts of Peptide M at pH 5.0 using solution NMR experiments.

Residue	NH (ppm)	C α H (ppm)	C β H (ppm)	Others (ppm)
I1	NA	3.882	1.954	NA
M2	8.717	4.516	2.021	γ -CH ₂ 2.558
D3	8.556	4.614	2.724	
R4	8.357	4.217	1.641	γ -CH ₂ 1.389 δ -CH ₂ 3.081
				NH 7.090
Y5	8.113	4.609	3.027/2.905	δ -H 7.049 ϵ -H 6.726
R6	8.056	4.356	1.735	γ -CH ₂ 1.538 δ -CH ₂ 3.154
				NH 7.191
V7	8.160	4.126	2.012	γ -CH ₃ 0.9080
R8	8.485	4.360	1.702/1.795	γ -CH ₂ 1.568 δ -CH ₂ 3.140
				NH 7.191
N9	8.585	4.630	2.793	
G10	8.440	3.930		
D11	8.207	4.650	2.774	
R12	8.240	4.237	1.654	γ -CH ₂ 1.442 δ -CH ₂ 3.019
				NH 7.020

I13	8.094	4.162	1.775	γ -CH 1.114
				δ -CH ₃ 0.805
W14	8.312	4.695	3.256/3.137	δ -H 7.207
				ε -H 7.581
				ζ 2-H 7.457
				ζ 3-H 7.167
				ε -NH ₃ ⁺ 7.128
I15	7.980	4.086	1.731	γ -CH 1.034
				δ -CH ₃ 0.856
R16	8.223	4.237	1.757	γ -CH ₂ 1.523
				δ -CH ₂ 3.126
L17	8.223	4.339	1.620	γ -CH 0.888
				δ -CH ₃ 0.841
R18	7.973	4.197	1.851	γ -CH ₂ 1.576
				δ -CH ₂ 3.167

Supplementary Table 2. Statistics for the 20 lowest energy NMR structures.

Parameter	Value
Distance and Angle Restraints	
Total NOEs	161
Intraresidual	73
Interresidual	88
Angles	9
Hydrogen bond restraints	--
Total restraints per residue	8.9
Statistics for Calculated Structures	
R.M.S.D. (Å)	
Backbone	0.59 ± 0.17
All Heavy Atoms	1.68 ± 0.31

Supplementary Table 3. NOEs used for calculations

assign (residue 1 and name HA) (residue 1 and name HB#) 3.0 1.2 0.6 !m
assign (residue 1 and name HA) (residue 1 and name HG#) 5.0 2.2 1.0 !w
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assign (residue 2 and name HA) (residue 3 and name HN) 2.5 0.7 0.4 !s
assign (residue 2 and name HB#) (residue 4 and name HB#) 5.0 2.2 1.0 !w
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assign (residue 3 and name HN) (residue 16 and name HN) 5.0 2.2 1.0 !w
```

Supplementary Table 4. Distances (Å) derived from the 20 lowest energy structural models
and the averaged, minimized NMR structure of Peptide M

MODEL #	Y5O-W14NH	Y5O-R16N ϵ H	Y5OH-R16N ϵ	Y5O-R16NH*	Y5OH-R16N*
1	6.1	9.3	9.7	9.7	10.9
2	5.9	6.4	7.2	8.2	9.2
3	6.2	5.4	5.2	1.5	3.1
4	6.0	9.3	9.7	7.9	9.6
5	6.4	2.8	3.7	1.4	3.1
6	6.3	4.2	4.2	1.5	3.1
7	6.3	8.5	6.9	5.5	5.4
8	6.5	5.1	5.3	1.4	3.2
9	6.7	5.7	4.2	3.7	3.3
10	6.2	4.9	4.4	2.9	2.9
11	6.5	5.1	4.8	7.3	6.8
12	6.4	7.0	6.0	7.4	7.0
13	6.4	8.4	7.5	9.5	9.0
14	6.9	7.8	8.0	7.7	8.8
15	6.7	4.8	4.4	2.7	2.8
16	6.7	6.5	6.1	5	5.3
17	6.0	9.2	7.6	7.1	6.5
18	6.6	6.9	5.7	5.7	5.8
19	6.6	4.9	5.1	1.4	3.1
20	6.3	6.7	6.0	7.3	7.1
AVE, MIN.	6.4	8.2	6.8	6.3	5.5

*For simplicity, only the distance to the closest–NH group (η^1 or η^2) of R16 is presented.

Supplementary Table 5. Distances (Å) derived from the 20 lowest energy structural models
and the averaged, minimized NMR structure of Peptide A¹

MODEL #	Y5O-H14NH	Y5O-R16N ϵ H	Y5OH-R16N ϵ	Y5O-R16NH*	Y5OH-R16N*
1	3.8	1.8	2.8	3.8	3.8
2	3.8	1.8	2.8	3.9	3.8
3	3.8	1.9	2.6	4.0	3.7
4	2.2	5.6	5.3	6.2	5.9
5	4.0	1.5	3.0	4.0	4.1
6	2.3	5.6	5.2	5.8	6.0
7	2.3	5.6	5.2	6.0	6.2
8	2.1	4.3	5.1	3.8	3.6
9	3.7	3.9	4.1	1.4	3.1
10	2.3	5.6	5.3	6.1	6.3
11	2.2	5.6	5.3	6.2	6.3
12	3.8	4.4	3.4	1.5	2.6
13	2.5	4.8	4.9	3.0	4.3
14	3.2	5.5	5.1	5.9	6.0
15	3.3	5.5	4.0	5.8	5.9
16	2.4	4.0	4.0	1.5	2.9
17	2.5	4.0	3.4	1.5	2.9
18	3.8	4.1	4.3	1.5	3.0
19	2.1	5.1	4.3	3.8	3.7
20	3.8	3.0	3.1	1.4	4.1
AVE, MIN.	4.0	1.6	2.9	3.8	3.9

*For simplicity, only the distance to the closest–NH group (η^1 or η^2) of R16 is presented.

Supplementary References

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